CHAPTER I

INTRODUCTION

1.1 Introduction to light scattering

Light scattering studies of small particulate matter produces results which have direct applications in atmospheric aerosol monitoring, aerosol generation processes, climate modelling, remote sensing, nanoscience, medical applications and most importantly astrophysical dust characterization. Laboratory modelling and simulation of interstellar dust particles and atmospheric aerosols, using synthesized analogue samples, is an efficient technique to measure their optical properties, widely distributed in shapes and sizes [1-4].

Light scattering is an outcome of light matter interaction phenomenon. It can be defined as the process of redirection of an incident beam due to the presence of an obstacle or due to variation of refractive indices in the propagation medium. The incident radiation induces individual dipoles in the medium to oscillate with its frequency, which in turn produces its own set of secondary radiations. The scattered field is additive i.e. the total intensity is a sum of all the scattered signals.

Light scattering can be broadly divided into two categories – (i) elastic and (ii) inelastic scattering. The former is the process in which the frequencies of incident and scattered waves remains same. While in the latter a change of frequency takes place during the light matter interaction event. Figure 1.1 shows a basic form of the light scattering phenomenon.

Further the theoretical explanation for the entire process of elastic light scattering may be divided into three basic domains according to the particle sizes as compared to that of the incident wavelength,

i. Particle size smaller as compared to wavelength (Rayleigh scattering region).
ii. Particle size comparable to the incident wavelength (Mie scattering region).
iii. Particle size is much larger than the incident wavelength (Geometrical optics region).

The scattering of light by aggregates may be single or multiple scattering. In single scattering the total scattered intensity is the sum of intensities scattered by each particle. If the particle separation is larger as compared to the radius of a single scatterer, no interference between light scattered by individual particles is observed (prominent in case of interstellar dust) [3, 5].

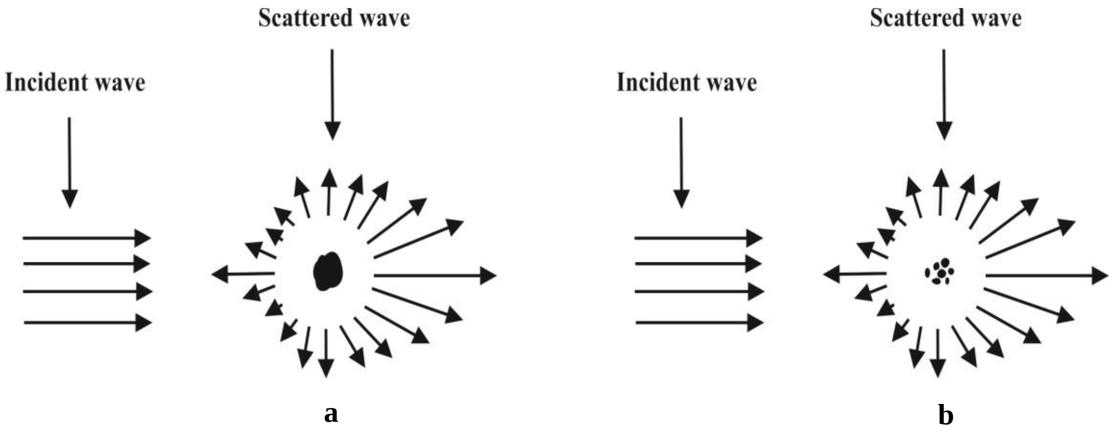

Figure 1.1 Light scattered by a (a) single particle and (b) multiparticle system.

In multiple scattering the secondary scattered fields from individual dipoles interacts with each other before being detected. In this case the light scattered by individual particles are not independently detected due to higher densities and the interference between scattered waves of individual particles must be considered [2].

1.2 Light scattering as an optical characterization tool

Extensive research on light scattering by different types of scatterers has been carried using different theoretical methods, simulation tools as well as experimental set ups with significant success. But due to limitations in addressing all the factors in a complex real situation, the theoretical and experimental results seldom match to high accuracies. The light scattering from particles that has been extensively investigated in the ultra-violet (UV) wavelengths, visible and infrared wavelengths includes aerosols and interstellar dust analogues.

The theoretical scattering characteristics of light by homogeneous spherical particles can be computed using Lorenz-Mie theory. But the natural and artificial particles are nonspherical or irregular for e.g. interstellar dust particles, atmospheric aerosols and microorganisms. The scattering properties of nonspherical particles differs dramatically from those of spherical or regularly shaped particles. So, nonsphericity must be thoroughly studied [3, 4]. Computationally dealing with complex and highly irregular shaped dust particles is a difficult problem due to the lack of adequate information about the shape, size, roughness, porosity, fluffiness and internal structures of those particles. The best approach is to try different advanced and efficient algorithms to model using a vast range of shapes and sizes supposed to constitute the complex dust systems.

One of the most important fields of optical characterization is the study of aerosol scattering properties. Aerosols are irregularly shaped particles naturally available in the atmosphere. They are either solid or liquid particles suspended in a gaseous medium or air. They are defining factors in influencing the radiative balance of the atmosphere and climate to a great extent [6]. The study of atmospheric aerosol has its applications in remote sensing, climate modelling and air quality monitoring [7-9].

Another important field for light scattering is the study of astrophysical dust. Dust grains determines the properties of interstellar medium [10]. The light scattering studies of dust present in the interstellar medium, protoplanetary disc, cometary comae and tails gives collective idea of their complex optical and radiative properties. The optical properties of dust grains directly affect the radiation fields from direct light sources observed with astronomical instruments. The laboratory analyses of interstellar dust analogues are absolutely vital for supporting the investigations based on observational data obtained with the ground and space based observatories.

Studies of interstellar and cosmic dust has confirmed that the majority of these particles have highly irregular and complex shapes [11, 12]. Realistic modeling of such type of particles requires visual evidence which is very difficult to acquire with a few exceptions like the STARDUST mission [13]. Recently, models of interstellar dust has been extensively studied by various research groups with carbonaceous dust (graphite and amorphous carbon particles), silicates (olivine, fayalite etc.), polycyclic aromatic hydrocarbons (PAHs), etc. [14-16]. Despite the numerous computational, observational and experimental studies, the physical and optical properties of dust particles are not properly known till date [17, 18]. Also laboratory based experimentations are required for interpretation of the observations [19].

The result of research works on analogue samples of naturally occurring aerosols and interstellar dust is a major contribution of the static light scattering technique. Light scattering instruments were developed and used to study a diverse kind of samples since the 1920s. The first instrument capable of measuring angular scattering patterns of particle systems called Tyndallmeter was developed by Tolman and Vliet in 1919. It was fitted with an electric light bulb as source and a Macbeth illuminometer as the detector to study liquid suspensions, smoke and mists [20]. Sinclair and La Mer developed another such instrument for particle sizing measurements of aerosols in 1949 [21]. Another such instrument was developed by Wyatt and Phillips in 1972 [22]. Grehan and Gouesbet (1980) used a setup to measure scattered light by a single levitated glass particle with an ionized argon laser beam [23]. Gucker et al. (1973) developed a single particle photometer to measure light scattering patterns through a full 360^0 range [24]. Perry et al. (1978) developed an advanced instrument capable of measuring Mueller matrix elements [2]. The instrument is capable of determining nonsphericity of particles applicable to astrophysical dust [25, 26]. Hovenier et al. used an instrumental setup to measure light scattering matrix elements at 441.6 nm and 632.8 nm [27].

Several micron and sub-micron sized aerosol and dust particle generators or nebulizers have been developed which significantly accelerated dust research using optical techniques [28, 29]. Regourd et al. used numerical simulation with mixtures of silicates and organics to imitate size and composition of cometary dust particles and concluded that mostly the dust grains are compact and fluffy [30]. Henning et al. reported the temperature influence on cosmic dust analogues of silicates and iron compounds [31]. Theoretical computations showed that the size-averaged values of scattering matrix elements depends on various physical parameters [32]. Such computations can also reproduce experimental results successfully [33].

The scattering matrix elements have been also studied at multiple wavelengths using combinations of goniometer setups and theoretical models for applications without direct contact [34]. Studies also demonstrated the advantages of using nonspherical particle models based on techniques like Discrete Dipole Approximation (DDA) and Geometric Optics Approximation (GOA) to simulate scattering properties of dust particles over conventional sphere models [35]. Zubko et al. developed a model of random irregular particles using DDA to study light scattering parameters that showed significant diversities in optical properties influenced by shape [36]. Gogoi et al. used an improved C program to compute light scattering by small particles and the effects of physical parameters like refractive index and size distribution on the scattering patterns [37]. Dubovik studied desert dust aerosol light scattering properties to reveal notable differences between spherical and nonspherical particles [38].

The refractive index and extinction coefficient of small particulate matter has prominent effects on their optical properties. Several studies have been performed to prove that changes induced by temperature and other physical parameters in optical constants could alter the predicted absorption and emission patterns [39]. The temperature dependence of the dielectric properties of interstellar carbonaceous and silica dust grains was studied by researchers [40]. The most important works which includes all the calculations of refractive index of carbonaceous and silicate materials for a wide wavelength range and variable temperatures are saved in a database named ‘the Jena-Petersburg database of optical constants’ (JPDOC) [41]. Roleau and martin tabulated the optical constants of amorphous carbon (a candidate of interstellar dust) [42]. Draine et al. reported the construction of dielectric functions for graphite and silicate mixtures using laboratory measurements and infrared observations [15]. A spectrometer with two illuminating laser sources were developed to measure, simultaneously, particle sizes and refractive indices [43].

The analogue samples of interstellar dust synthesized in the laboratory are complementary part of light scattering studies. Such readily available particles could be used directly in the experimental characterizations providing valuable insights into the dust grain properties. Rotundi et al. systematically presented a number of synthesis techniques for astrophysical dust analogue of carbon and mineral silicates [44]. Pinnick et al. generated aerosol particles in the laboratory for in situ measurements [45].

Recent studies revealed the diverse composition, crystal structure and size of interplanetary dust particles [46-51]. The Hubble space telescope [52] indicated that interstellar medium contains amorphous silicate, carbon, graphite and ice particles along with carbonates and oxides [53-57]. Compositions and density of grains are significantly different in different regions in space. For example, the meteoric dust particles are mainly composed of anhydrous oxides of silicon, magnesium, aluminium, iron and calcium as compared to dust particles of graphite and silicates in the interstellar medium [19, 58]. The most extensively used representative of extraterrestrial dust particles are magnesium and iron silicates along with graphite [59]. But an accurate interstellar dust model that fits the observed emission and extinction features simultaneously is absent. So these problems needs to be addressed extensively [14]. The interstellar absorption and extinction curves could be reproduced in numerical modeling by taking into account the effects of physical material properties [60, 61]. But small oscillations and features in the micro scale could only be addressed by considering additional variable like orientations as compared to the conventional ones [62-65].

1.3 Computational tools

A number of theoretical tools and algorithms which provide sufficient support for experimental light scattering studies of regular and ordered particles are available. The Mie scattering theory is one of the best known tool that gives exact solutions to the light scattering problem of perfect spheres and spheroidal particles. Similarly the T- matrix approach is advantageous for some particular standard shapes. But particles encountered in realistic environments are not always spherical, but are nonspherical, non-rotational, non-symmetric, inhomogeneous, coated, chiral or anisotropic [4]. In order to study highly irregular particles found in terrestrial and extraterrestrial environments e.g., mineral and soot aerosols, interstellar and cometary dust grains, algorithms like superposition T-matrix method (TMM), Finite Fifference Time Domain (FDTD), Discrete Dipole Approximation (DDA), etc., along with some modifications are required [66]. Although unavailability of an exact algorithm to address the nonsphericity of particulate matter still persists, some of the developed methods are relatively successful in supporting experimental studies to some extent for e.g. DDA, FDTD etc. Importantly, the computational tools and experimentations require to be complimentary to each other to make simulations effective [67].

1.3.1 Computational tools for spherical particles (Mie theory)

Mie theory is the most effective numerical algorithm in determining the absorption and emission properties of small particulate matter with spherical shapes. Although this theory provides exact solutions to only spheres, it’s also widely used to compute the optical properties of nonspherical particles to a lesser extent. Its simplicity has led to wide use in many numerical techniques [2, 3].

The analysis of the properties of radiative transfer equations requires extensive formalism of analytical methods to find the scattered electric and magnetic fields subjected to boundary conditions. These calculated values must be accurate enough to reproduce optical spectral patterns observed in case of light matter interaction phenomenon. Mie theory satisfies all those important criterions of an efficient computational tool for spherical shapes. The only restriction is that it requires the particle size parameter to be $2\pi r/\lambda \approx 1$ ($r \rightarrow$ radius of the particle) with only real values of the refractive index, i.e. non-absorbing particles.

1.3.2 Computational characterization techniques for nonspherical particles

The computational techniques involving the investigation of nonspherical particles are generally restricted by the particle size parameter (size of the scatterer relative to the incident wavelengths). These methods require rigorous mathematical calculations involving scattered radiation fields considering the irregularities in shapes and particle orientation directions. Some algorithms like the finite-difference method and finite element method are efficient but the computational requirements are unaffordably high, as the particle size increases. Another such method is the null field method. Some of the method are briefly explained in this section.

1.3.2.1 Finite Element Method (FEM)

The finite element method provides approximate solutions to elliptic partial differential equations or boundary value problems involving light matter interaction events. This method simplifies the elliptic partial differential problem by converting the equations into simple algebraic forms. To calculate the scattered fields at particle surface it numerically solves the vector Helmholtz equation, constraining the system with applicable boundary conditions [68, 69].

The principal advantage of FEM is that it facilitates nonspherical and inhomogeneous particles to be considered for calculation of radiation fields. It is also easy to execute and is free of the singular-kernel problems involving integral equation methods. But one of the disadvantage is that it is computationally time consuming compared to the methods that provides exact solutions. And is difficult to apply for particles beyond size parameters of 10.

1.3.2.2 Finite-Difference Time-Domain method (FDTD)

This technique is applied in the microwave region. Its applicability is immensely wide, ranging from study of scattering from metals to dielectrics and antennas. One major utility is the study of radiation effects on human body. The technique was first proposed by K. Yee [70, 71]. FDTD is based on discretizing the Maxwell’s equations.

FDTD directly solves Maxwell's time dependent curl equations [70]. The scattering particles are treated using a set of absorbing boundary conditions and the scattering properties are calculated in free space [4]. The discretization significantly reduces memory requirements as it reduces the number of linear equations to be solved. It holds significant advantage over other numerical codes in terms of allowed size parameter.

1.3.2.3 Discrete Dipole Approximation (DDA)

Discrete Dipole Approximation (DDA) facilitates the calculation of scattering and absorption by nonspherical shapes. It is advantageous mainly for targets comparable to incident wavelength. DDA can calculate scattering properties for particles satisfying '$2\pi\ a_{eff}\ /\ \lambda \leq 25$' ($a_{eff} \rightarrow$ effective particle size) for refractive index (m) smaller than unity i.e. ($|m - 1| \leq 2$). Apart from single particle, the 4×4 Mueller matrix can be also computed for periodic targets. It is the most widely used code to calculate scattering by terrestrial and extraterrestrial dust because of its flexibility regarding shapes. DDA is also capable of computing scattered fields for inhomogeneous and anisotropic particles [72].

DDA (or coupled dipole method) involves approximating the target particle by a number (N) of polarizable points called dipoles [73]. It considers all possible internal interactions of the incident field and the radiation scattered within the particle volume. It involves rigorous solution to N-partial differential equations containing the scattered field information of all the radiating dipoles. And then specifies location to all the point dipoles to whole volume of the scattering particle and thereby account for irregularities in the geometry. But the number of dipoles must not exceed a value of 10^6 owing to CPU computational powers. Recent developments in DDA incorporates complex-conjugate gradient (CCG) methods and fast-Fourier-transform (FFT) which significantly reduces the computation time. A user friendly FORTRAN© code of DDA 'DDSCAT' has been developed by Draine and Flatau [74] as an open source code. Modern scientific workstations allows the particle size parameters to be extended for a range of $x \leq 10$ introducing sufficiently large number of dipoles [75, 76]. The main disadvantages of the technique is that it is relatively time consuming and the numerical accuracy decreases with increasing particle sizes. Also with increasing number of dipoles the whole calculation needs to be repeated for each new incident directions (for DDA with CGM-FFT) [75-77].

1.3.2.4 T-Matrix Method (TMM)

The null-field method or T-matrix method is a technique for computing light scattering by conducting and dielectric particles, especially with some regular geometries [79, 80]. The T-Matrix approach can treat a number of arbitrary geometries from multilayered and composite particles to chiral particles [81, 82]. It is also used in study of multiple scattering by targets [83]. Till date its numerical stability has been vastly improved in computations for complex shapes [84]. A number of numerical algorithms based on T-Matrix are available for computations [67, 85, 86]. T-Matrix can compute scattering properties of both homogeneous and inhomogeneous particles, isotropic and anisotropic materials, conducting spheres with axisymmetric surfaces, layered particles and nonspherical particle clusters.

1.3.2.5 Geometric Optics Approximation (GOA)

The geometric optics approximation (GOA) also known as ray tracing method is employed to compute light scattering properties of very large particles compared to incident light wavelengths. GOA assumes a collection of parallel rays to replace an incident electromagnetic beam. Later Snell’s law in combination with Fresnel’s equations are used to model the light matter interaction taking place in the particle. The scattered rays are sampled over the particle projections using diffraction patterns of incident waves, giving a solution to the scattering problem. It is straightforward for spheres but couples with Monte Carlo simulations to produce scattering patterns for nonspherical shapes [4, 87, 88]. GOA is particularly not restricted by particle shapes but less reliable due to its approximate formalism.

1.3.3 Computational Codes in public domain

The available computational tools used to treat the nonspherical particle problems are not applicable to all shapes and orientations. These methods are application oriented, restricted by particle geometries and size parameters, even to some extent depends on the complex refractive index. Some advantages of one technique may be observed over another in particular cases depending on the situations and physical parameters. It’s also an extremely difficult task to compare all the techniques or accuracy and efficiency as they seldom find applications in similar kind of computations. Other than Mie theory, DDA and T-Matrix are considered to be standardized in this case. Standard results for spheroids and other standard shapes were reported a number of times [89, 90]. But considering the realistic particulate matter samples widely varying in shapes and sizes, the accuracy of computational techniques are always put into test while treating atmospheric aerosols and dust.

Several efficient software packages are available to compute light scattering parameters using Mie theory, TMM, FDTD, DDA etc. The particular software package DDSCAT7.3, used in this work is based on DDA. Some of the popular DDA codes are DDSCAT, DDSCAT.CPP, ADDA, OPENDDA, etc. [66]. DDSCAT, by Bruce T. Draine (Dept. of Astrophysical Sciences, Princeton University) and Piotr J. Flatau (Scripps Institution of Oceanography, UCSD) in FORTRAN, is one of the most popular computer codes used for electromagnetic scattering calculations by nonspherical particles [72-74, 91]. Some of the most popular and widely used codes available in the public domain are presented in this section.

1.3.3.1 T -matrix code

It is a computer program available in the FORTRAN language using the null field method to solve electromagnetic scattering problem for fixed and randomly oriented scatterers. Uniform orientation distribution functions are used to compute scattering and absorption properties of scattering particles. The input parameters for this code are incident wavelength, particle radius, refractive indices of the particle and medium (nonabsorbing). The output parameters are scattering angle (θ) and scattering matrix elements, scattering efficiency (Q_{sca}), extinction efficiency (Q_{ext}), single scattering albedo (a) and asymmetry parameter (g).

1.3.3.2 DDSCAT code

DDSCAT 7.3 is the latest version of original FORTRAN-90 code based on DDA, which can calculate the electromagnetic scattering and absorption properties of particles with arbitrary geometries and complex refractive index values. It can be applied to both scattering by single particles, particle systems and 1-d and 2-d periodic finite targets. A number of particle shapes (for e.g., ellipsoids, hexagonal prisms, finite cylinders etc.) are predefined in different functions and subroutines in the code. The most important inclusion in DDSCAT is the user friendly procedure of importing any type of irregular and complex target geometries in the form of a 'shape.dat' file directly into the code. It also allows user to modify the main 'executable parameter file' with flexibility regarding most of the input parameters (either to apply restrictions or assign new values). The number of directions of particle orientation in the scattering plane and allowed scattering directions can be modified very easily. The main difficulty lies in the generation of external target geometries to replicate dust particles. It also calculates all the near and far field values of electric and magnetic fields for the scattering particle, carried out by a subroutine 'ddapostprocess'.

DDSCAT is the most versatile and flexible computational tool used to calculate the optical properties irregular dust particles (terrestrial and extra-terrestrial). There is some restrictions regarding the particle sizes as compared to the incident wavelengths which requires that the interdipole separation (*d*) must be small compared to structural dimensions in the target and must also be the smaller or almost equal to the incident wavelength. There is a condition called 'DDA condition' which must be satisfied for accurate computation of the scattering matrix elements [74],

$$|m|kd < 1 \tag{1.1}$$

where m is the complex refractive index and $k \equiv \frac{2\pi}{\lambda}$, λ is the incident wavelength in vacuum. For calculations demanding more computational accuracy (e.g., radar or lidar applications) the condition becomes more critical.

i.e. $|m|kd < 0.5$. And the particle size parameter is the only factor that limits DDSCAT [74, 75].

1.4 Light scattering experimentations

1.4.1 Static light scattering

Two techniques are generally employed to investigate light scattering properties of small particulate matter.

Static light scattering measures the average scattered intensity of particles in fluids or solution by integrating the scattered signal over a period of time. The output is then used to determine particle size and molecular weight. The intensity is very sensitive to variations in size of the solutes, so that it is advantageous to investigate aggregation in scattering media.

Dynamic light scattering monitors the fluctuations of scattered photons over very short time intervals from the sample. The output is a direct indication of the Brownian movement of particles and their diffusion characteristics which can then be used to determine particle size.

The technique used in this thesis work is **static light scattering**. The properties of static light scattering are,

1. It’s an optical characterization technique in which the scattered light intensity is measured as a function of scattering angle.
2. The study of spatial scattering dependency of small particulate matter helps in detection of scattering particles in a medium and to understand the complex mechanism of radiation transfer.
3. In the simplest form the static light scattering setups used for scattering profile calculations, either consists of a movable single detector or multi angle array sensors that facilitates the detection and measurement of intensities at all the points or angles of interest simultaneously.

1.4.2 Experimental measurements of scattering matrix elements

The restriction that reduces efficiency of light scattering computations are not applicable to experimental measurements of the scattering matrix. But the technical difficulties involving measurement of very small particles at visible, infrared and ultraviolet wavelengths are the source parameters and detector sensitivities. Also special care should be taken for selective absorption of particular wavelengths in the propagating medium. Another factor which requires special treatment is contamination of scattering particles with dust present in the medium. The problem magnifies when the dust particles are of similar sizes to the target. Also there is a tendency of particle aggregations during the process of particle delivery to the path of incident beam.

In a typical light scattering experimental setup a light beam basically from a laser or xenon light source is used. The beam passes through polarizers and interacts with particles either in suspensions or in a jet stream. The angular light scattering patterns are detected by spatially distributed photodetectors (photodiode or photomultiplier tube), fitted with analyzers for selective acquisition of polarized signals. The analyzers are basically linear or circular polarizers and quarter wave plates. The main difficulty is that the orientation of these active optical components must be perfect respect to the scattering plane for recording a particular scattering event in the scattering volume. Another limitation of the experimental setups is its inability to measure the scattered light at extreme angles i.e. close to 0^{o} and 180^{o} respectively, mainly due to safety of highly sensitive photodetectors [3, 4]. The finite aperture problem also persists for extinction cross section measurements due to stray signals. Most of the experimental arrangements uses only unpolarized incident light to measure two of the Mueller matrix elements, the volume scattering function and degree of linear polarization. This is because of considering the nature of natural and astrophysical light sources like stars, these elements are sufficient to measure majority of optical and physical properties of a particular kind of scatterer. The complexities of using a large number of optical components and the high demand of adequate care to ensure perfect alignment and calibration leads to the fact why the full scattering matrix is less frequently measured.

The physical properties of particulate matter that determines their light scattering behaviors and patterns are size, refractive index, and density along with the particle shape, geometry, and surface roughness [3, 4, 92]. In case of slightly larger particles, sharp edges and small features also influence their optical properties mainly for irregularly shaped particles. The scattering matrix elements can be measured successfully in the laboratory with simple lasers and or other light sources and photodetectors [27].

The light scattering instruments essentially measure the intensity and polarization of the scattered light. These results are then used to interpret size, shape and size distributions of the scattering particles.

The most basic form of light scattering instruments are the nephelometers. It is an instrument used for measuring angular variations in intensities and polarization of scattered radiation [2]. Its importance is the determination of particle sizes and shapes from the angular scattering patterns [93-95].

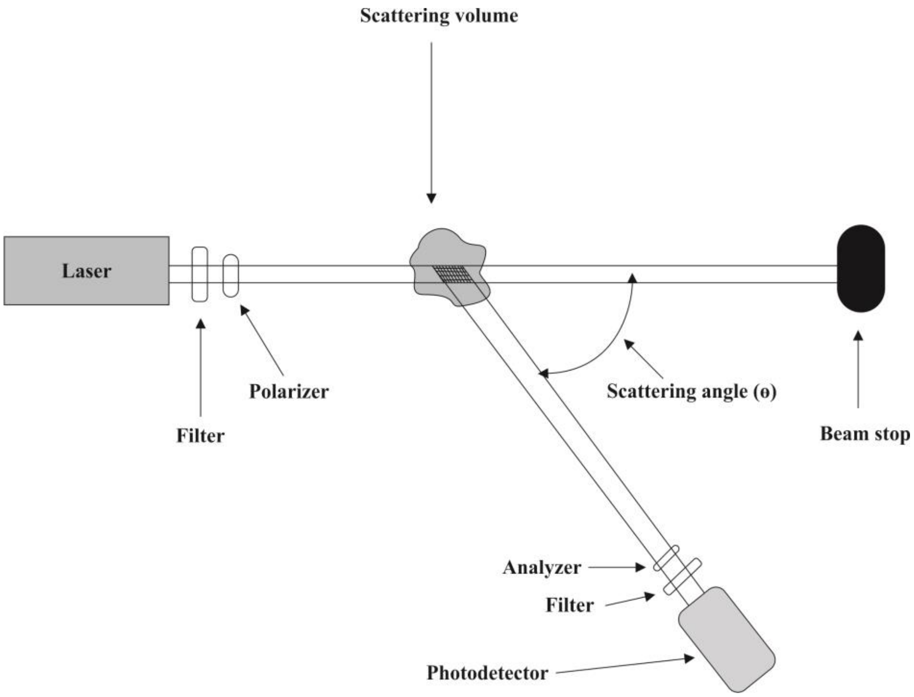

Figure 1.2 Nephelometer setup.

As shown in the Figure 1.2, a simple nephelometer consists of a light source with collimators and slits. A number of active optical components- neutral density filters, color filters and polarizers (linear, circular and quarter wave plates) are employed to control the color, intensity and polarization states of the laser light. The detector is basically a photodiode or a photomultiplier tube. The system can rotate over the scattering plane in the range of 0^0 to 180^0 respectively, with variable angular resolution as demanded by the experiments. The detector is fitted with suitable lenses, filters and analyzers. These setups are highly stable and successfully measures the optical properties of particles. But with changes in scattering angle the scattering volume changes (intersection region of the incident wave with the detector field of view). A beam stop is used at the extreme ends of the setup to absorb the directly incident light thus providing a dark background for greater sensitivity of the relatively weak scattered light by the detectors.

1.5 Origin of the problem

In recent years various theoretical and experimental calculations using Mie theory, Finite difference time domain method (FDTDM), Waterman’s T-matrix method, Discrete dipole approximation (DDA), Geometrical optics approximation (GOA) etc. have been carried out in an attempt to explain experimental and observed light scattering properties of dust particles. But due to some inadequacies in addressing all the factors in a complex real situation, the theoretical and experimental results seldom fit arguably at higher degrees of accuracy. Numerical techniques are inadequate without modifications, to provide strong evidences about the combined effects of a large number of physical variables as observed in case of dust particles.

1.6 Objectives of the work

1. Design, development and modifications of a light scattering characterization setup based on laser probes and photodetectors.
2. Development of computational tools based on DDA for simulation of physical and light scattering properties of a variety of samples (aerosols, dust, hydrosols and biological cells).
3. Comparative analyses of the calculated and experimental light scattering parameters of interstellar graphite dust analogue samples.
4. Synthesis and comparative study of scattering parameters of interstellar silicate dust analogue sample (Fayalite (Fe_2Si0_4)).
5. Comparative analyses of scattering parameters of silica as atmospheric aerosol analogue for remote sensing and medical applications.
6. Study of graphite and fayalite dust analogue mixture to develop models to reproduce experimental results.

1.7 Outline of the thesis

This PhD thesis is a detailed description of the modeling and simulation studies of highly irregular particulate matter in the form of analogue samples for interstellar dust and atmospheric aerosols, using user generated shapes.

The light scattering properties of small particulate matter in the Mie regime are calculated using theoretical computational techniques Mie theory and DDA. Experimental measurements with a laboratory set up using a laser based probe and suitable detector system have been performed. Different types of micron and submicron sized particles are investigated having multidispersed size distributions to represent their states in naturally available forms.

Realistic models are designed and the theoretical computation of light scattering parameters namely phase function, linear polarization, single-scattering albedo, asymmetry parameter, cross-sections of extinction and absorption for different wavelengths are performed. A comparative analysis of the theoretically calculated and experimentally measured light scattering patterns at various incident wavelengths are also conducted. In the computational models several irregular shapes are generated which were found to be very common in the scanning electron microscopy (SEM) images of real samples used in the laboratory measurements and subsequently their light scattering properties are computed.

This thesis consists of seven chapters and a general introduction (current chapter) including definition of the problem and literature review.

In **chapter II** the theories of light scattering and a short theoretical background of DDA is discussed along with mathematical formalism. The mathematical calculation techniques of scattering matrix elements are provided in details with the size and shape averaging equations.

In **chapter III** detailed description of the developed computational technique is provided. Details of the experimental setup used in the study is also presented in the chapter. The experimental validation and calibrations of the laboratory setup is given with explanations.

The **chapter IV** provides a description of the computational and experimental light scattering studies of interstellar dust analogue samples of graphite and fayalite. In the first part, the light scattering properties of shape and size distributed graphite samples are calculated and conclusive evidences were found about the particle shape and surface roughness effects on the size averaged and normalized values of scattering parameters. In the second part computational and experimental studies of fayalite is presented. The findings are important keeping in mind the fact that it is the rarest studied species of silicate dust, due to limited availability in the earth’s crust.

In **chapter V** the light scattering studies of silica is provided in detail. The light scattering properties of silica microparticles are performed, due to its importance as an atmospheric aerosol and drug delivery agent in medications. These studies provided important clues about the modeling techniques to detect and characterize the properties of highly irregular unknown scatterers with complex optical properties.

Chapter VI provides the modeling and simulation studies of a mixture graphite and fayalite. A comparative analysis of the theoretical and experimental results of shape and size averaged scattering parameters shows the effects of changing the percentage composition, number of dipoles, and number of directions considered for orientational averaging. These demonstrates a well-defined model to calculate the light scattering parameters of dust aggregates with two or three constituent elements.

Finally in the **chapter VII** the conclusions about the developed computational models are provided along with explanations for acquired results and possible reasons for theoretical and experimental errors. The limitations of the work and future directions are also included.

References

1. Ahmed, G. A. *Design considerations of a laser based air quality monitoring system coupled to a microprocessor linked data recording and processing unit*, PhD thesis, Gauhati University, Guwahati, 2001.
2. Bohren, C. F. and Huffman, D. R. *Absorption and Scattering of Light by Small Particles*, John Wiley & Sons Inc, New York, 1983.
3. Van De Hulst, H. C. *Light Scattering by small particles,* John Wiley & Sons, New York, 1957.
4. Mishchenko, M. I., Hovenier, J. W., and Travis, L. D. (editors) *Light Scattering by Nonspherical Particles: Theory, Measurements, and Applications,* Academic, San Diego, California, 2000.
5. Hansen, J. E. and Travis, L. D. *Light scattering in planetary atmospheres. Space Sci. Rev.,* 16(4):527-610, 1974.
6. Fierz-Schmidhauser, R., Zieger, P., Gysel, M., Kammermann, L., DeCarlo, P.F., Baltensperger, U. and Weingartner, E., Measured and predicted aerosol light scattering enhancement factors at the high alpine site Jungfraujoch. *Atmospheric Chemistry and Physics*, 10(5):2319-2333, 2010.
7. Mishchenko, M.I., Lacis, A.A., Carlson, B.E. and Travis, L.D., Nonsphericity of dust-like tropospheric aerosols: Implications for aerosol remote sensing and climate modeling. *Geophysical Research Letters*, 22(9):1077-1080, 1995.
8. Charlson, R.J., Horvath, H. and Pueschel, R.F., The direct measurement of atmospheric light scattering coefficient for studies of visibility and pollution. *Atmospheric Environment,* 1(4):469-478, 1967.
9. Solomon, S. ed., *Climate change 2007-the physical science basis: Working group I contribution to the fourth assessment report of the IPCC (4).* Cambridge university press, Cambridge, 2007.
10. Draine, B.T. Interstellar Dust Grains. *Ann.Rev.Astron.Astrophys.*, 41:241-289, 2003.
11. Mishchenko, M.I., Travis, L.D., Kahn, R.A. and West, R.A., Modeling phase functions for dustlike tropospheric aerosols using a shape mixture of randomly oriented

polydisperse spheroids. *Journal of Geophysical Research: Atmospheres*, 102(D14):16831-16847, 1997.

12. Brownlee, D. E., Pilachowski, L., Olszewski, E., Hodge, P. W., Analysis of interplanetary dust collections. In: Halliday I. and McIntosh B. A. (Eds.), *Solid Particles in the Solar System,* Proceedings of the Symposium: International Astronomical Union, 90, D. Reidel, Dordrecht, Ottawa, Canada, August 27-30, pages 333-342, 1979.
13. Burnett, D.S., NASA Returns Rocks from a Comet. *Science*, 314(5806):1709-1710, 2006.
14. Zubko, V., Dwek, E., and Arendt, R.G., Interstellar Dust Models Consistent with Extinction, Emission, and Abundance Constraints. *Astrophys.J.Suppl*, 152(2):211-249, 2004.
15. Draine, B. T., and Lee, H. M. Optical properties of interstellar graphite and silicate grains. *The Astrophysical Journal*, 285:89-108, 1984.
16. Draine, B.T., and Li., A., Infrared emission from interstellar dust. iv. the silicate-graphite-pah model in the post-spitzer era. *The Astrophysical Journal*, 657(2):810-837, 2007.
17. Wright, E. L., Long-wavelength absorption by fractal dust grains. *Astrophys. J.*, 320:818-824, 1987.
18. Mathis, J.S. and Whiffen, G. Composite interstellar grains. *Astrophysical Journal Part1,* 341:808-822, 1989.
19. Henning, T., and Mutschke, H. Optical properties of cosmic dust analogs: A review. *J. Nanophoton*, 4(1):041580, 2010.
20. Tolman, R.C. and Vliet, E.B., A tyndallmeter for the examination of disperse systems. *Journal of the American Chemical Society*, 41(3):297-300, 1919.
21. Sinclair, D. and La Mer, V.K., Light Scattering as a Measure of Particle Size in Aerosols. The Production of Monodisperse Aerosols. *Chemical reviews*, 44(2):245-267, 1949.
22. Wyatt, P.J. and Phillips, D.T., A new instrument for the study of individual aerosol particles. In *Aerosols and Atmospheric Chemistry*, 127-137, 1972.

23. Grehan, G. and Gouesbet, G., Optical levitation of a single particle to study the theory of the quasi-elastic scattering of light. *Applied optics*, 19(15):2485-2487, 1980.
24. Gucker, F.T., Tůma, J., Lin, H.M., Huang, C.M., Ems, S.C. and Marshall, T.R., Rapid measurement of light-scattering diagrams from single particles in an aerosol stream and determination of latex particle size. *Journal of Aerosol Science*, 4(5):389-404, 1973.
25. Perry, R.J., Hunt, A.J. and Huffman, D.R., Experimental determinations of Mueller scattering matrices for nonspherical particles. *Applied Optics*, 17(17):2700-2710, 1978.
26. Kerker, M., Light scattering instrumentation for aerosol studies: An historical overview. *Aerosol Science and Technology,* 27(4):522-540, 1997.
27. Hovenier, J.W., Volten, H., Munoz, O., Van der Zande, W.J. and Waters, L.B.F.M., Laboratory studies of scattering matrices for randomly oriented particles: potentials, problems, and perspectives. *Journal of Quantitative Spectroscopy and Radiative Transfer,* 79:741-755, 2003.
28. Berglund, R.N., & Liu, B.Y.H. Generation of monodisperse aerosol standards. *Environ. Sci. Technol.*, **7**(2):147-153, 1973.
29. Hahn, D.W., et al. Aerosol generation system for development and calibration of laser-induced breakdown spectroscopy instrumentation. *Rev. Sci. Instrum*., 72(9):3706, 2001.
30. Levasseur-Regourd, A.C., Mukai, T., Lasue, J. and Okada, Y., Physical properties of cometary and interplanetary dust. *Planetary and Space Science,* 55(9):1010-1020, 2007.
31. Henning, Th., and Mutschke, H. Low-temperature infrared properties of cosmic dust analogues. *Astron. Astrophys*., 327:743–754, 1997.
32. Vilaplana, R., Moreno, F. and Molina, A., Study of the sensitivity of size-averaged scattering matrix elements of nonspherical particles to changes in shape, porosity and refractive index. *Journal of Quantitative Spectroscopy and Radiative Transfer,* 100(1-3):415-428, 2006.
33. Munoz, O., Volten, H., De Haan, J.F., Vassen, W. and Hovenier, J.W., Experimental determination of the phase function and degree of linear polarization of El Chichon and

Pinatubo volcanic ashes. *Journal of Geophysical Research: Atmospheres*, 107(D13): ACL 4-1–ACL 4-8, 2002.

34. Ding, H., Lu, J.Q., Brock, R.S., McConnelll, T.J., Ojeda, J.F., Jacobs, K. and Hu, X.H., Angle-resolved Mueller matrix study of light scattering by B-cells at three wavelengths of 442, 633, and 850 nm. *Journal of biomedical optics*, 12(3):034032, 2007.
35. Bi, L., Yang, P., Kattawar, G.W. and Kahn, R., Modeling optical properties of mineral aerosol particles by using nonsymmetric hexahedra. *Applied optics*, 49(3):334-342, 2010.
36. Zubko, E.S. Light scattering by irregularly shaped particles with sizes comparable to the wavelength. *Light Scattering Reviews*, 6:39-74, 2012
37. Gogoi, A., Choudhury, A. and Ahmed, G.A., Mie scattering computation of spherical particles with very large size parameters using an improved program with variable speed and accuracy. *Journal of Modern Optics*, 57(21):2192-2202, 2010.
38. Dubovik, O., Sinyuk, A., Lapyonok, T., Holben, B.N., Mishchenko, M., Yang, P., Eck, T.F., Volten, H., Munoz, O., Veihelmann, B. and Van der Zande, W.J., Application of spheroid models to account for aerosol particle nonsphericity in remote sensing of desert dust. *Journal of Geophysical Research: Atmospheres*, 111(D11), 2006.
39. Jellison, Jr. G.E. and Modine, F.A. Optical functions of silicon at elevated temperatures. *J. Appl. Phys*., 76(6):3758, 1994.
40. Kocifaj, M., Klačka, J. and Horvath, H., Temperature-influenced dynamics of small dust particles. *Monthly Notices of the Royal Astronomical Society*, 370(4):1876-1884, 2006.
41. Jäger, C., Il'in, V.B., Henning, T., Mutschke, H., Fabian, D., Semenov, D.A. and Voshchinnikov, N.V., A database of optical constants of cosmic dust analogs. *Journal of Quantitative Spectroscopy and Radiative Transfer*, 79:765-774, 2003.
42. Rouleau, F. and Martin, P.G., Shape and clustering effects on the optical properties of amorphous carbon. *The Astrophysical Journal*, 377:526-540, 1991.
43. Szymanski, W.W., An Innovative Approach to Optical Measurement of Atmospheric Aerosols, Y.J Kim and U. Platt, eds., *Advanced Environmental Monitoring, Springer*, 167-178, 2008

44. Rotundi, A., Brucato, J.R., Colangeli, L., Ferrini, G., Mennella, V., Palomba, E. and Palumbo, P., Production, processing and characterization techniques for cosmic dust analogues. *Meteoritics & Planetary Science*, 37(11):1623-1635, 2002.
45. Pinnick, R.G., Rosen, J.M. and Hofmann, D.J., Measured light-scattering properties of individual aerosol particles compared to Mie scattering theory. *Applied optics*, 12(1):37-41, 1973.
46. Westphal, A.J., Stroud, R.M., Bechtel, H.A., Brenker, F.E., Butterworth, A.L., Flynn, G.J., Frank, D.R., Gainsforth, Z., Hillier, J.K., Postberg, F. and Simionovici, A.S., Evidence for interstellar origin of seven dust particles collected by the Stardust spacecraft. *Science*, 345(6198):786-791, 2014.
47. Mishchenko, M.I., Travis, L.D., Kahn, R.A. and West, R.A., Modeling phase functions for dust like tropospheric aerosols using a shape mixture of randomly oriented polydisperse spheroids. *Journal of Geophysical Research: Atmospheres*, 102(D14):16831-16847, 1997.
48. Brownlee, D.E., Pilachowski, L., Olszewski, E. and Hodge, P.W., January. Analysis of interplanetary dust collections. In *Symposium-International Astronomical Union*, volume 90, pages 333-342, Cambridge University Press, 1980,
49. Vaidya, D.B., Gupta, R. and Snow, T.P., Composite interstellar grains. *Monthly Notices of the Royal Astronomical Society*, 379(2):791-800, 2007.
50. Kissel, J., Glasmachers, A., Grün, E., Henkel, H., Höfner, H., Haerendel, G., Von Hoerner, H., Hornung, K., Jessberger, E.K., Krueger, F.R. and Möhlmann, D., Cometary and interstellar dust analyzer for comet Wild 2. *Journal of Geophysical Research: Planets*, 108(E10), 2003.
51. Giese, R. H., Weiss, K., Zerull, R. H., and Ono, T., Large fluffy particles: a possible explanation of the optical properties of interplanetary dust. *Astron. Astrophys.,* 65:265-272, 1978.
52. Savage, B. D., and Sembach, K. R. Interstellar abundances from absorption-line observations with the Hubble Space Telescope. *Annual Review of Astronomy and Astrophysics*, 34:279-329, 1996.

53. Jones, A. P. Interstellar and circumstellar grain formation and survival. *Phil. Trans. R. Soc. Lond. A*, 359(1787):1961-1972, 2001.
54. Rai, R. K., and Rastogi, S. Modelling anomalous extinction using nanodiamonds. *Mon. Not. R. Astron. Soc.,* 423(3):2941-2948, 2012.
55. Draine, B. T. Interstellar Dust Grains, *Annual Review of Astronomy and Astrophysics.* 41:241-289, 2003.
56. Dai, Z.R., Bradley, J.P., Joswiak, D.J., Brownlee, D.E., Hill, H.G.M. and Genge, M.J., Possible in situ formation of meteoritic nanodiamonds in the early solar system. *Nature*, 418(6894):157, 2002.
57. Mann, I. Interstellar dust in the solar system. *Annual Review of Astronomy and Astrophysic*, 48:173-203, 2010.
58. Jones, A.P., Interstellar and circumstellar grain formation and survival. *Philosophical Transactions of the Royal Society of London A: Mathematical, Physical and Engineering Sciences*, 359(1787):1961-1972, 2001.
59. Kocifaj, M. *Lecture Notes: Light scattering by Small Particles Atmospheric Optics and Astrophysical Application Part I–Theory,* Institute of Experimental Physics, University of Vienna and Astronomical Institute,Slovak Academy of Sciences, 2007.
60. Voshchinnikov, N.V., Interstellar extinction and interstellar polarization: Old and new models. *Journal of Quantitative Spectroscopy and Radiative Transfer*, 113(18):2334-2350, 2012.
61. Zubko, E., Shkuratov, Y. and Videen, G., Effect of morphology on light scattering by agglomerates. *Journal of Quantitative Spectroscopy and Radiative Transfer*, 150:42-54, 2015.
62. Wheeler, V.M., Randrianalisoa, J., Tamma, K. and Lipiński, W., Spectral radiative properties of three-dimensionally ordered macroporous ceria particles. *Journal of Quantitative Spectroscopy and Radiative Transfer*, 143:63-72, 2014.
63. Dabrowska, D.D., Muñoz, O., Moreno, F., Ramos, J.L., Martínez-Frías, J. and Wurm, G., Scattering matrices of Martian dust analogs at 488 nm and 647 nm. *Icarus*, 250:83-94, 2015.

64. Lumme, K., and Rahola, J. Comparison of light scattering by stochastically rough spheres, best-fit spheroids and spheres. *J. Quant. Spectrosc. Rad. Transfer,* 60(3):439-450, 1998.
65. Zubko, E., Muinonen, K., Muñoz, O., Nousiainen, T., Shkuratov, Y., Sun, W. and Videen, G., Light scattering by feldspar particles: comparison of model agglomerate debris particles with laboratory samples. *Journal of Quantitative Spectroscopy and Radiative Transfer*, 131:175-187, 2013.
66. SCATTPORT. Weblink: http://www.scattport.org/. Date accessed: 25th January, 2018.
67. Doicu, A., Wriedt, Th. and Eremin, Y.A. *Light Scattering by Systems of Particles Null-Field Method with Discrete Sources: Theory and Programs*, Springer Series in Optical Sciences, 124, Springer-Verlag Berlin Heidelberg, 2006.
68. Morgan, M. and Mei, K., Finite-element computation of scattering by inhomogeneous penetrable bodies of revolution. *IEEE Transactions on Antennas and Propagation,* 27(2):202-214, 1979.
69. Silvester, P. P., and Ferrari, R. L. *Finite Elements for Electrical Engineers*, Cambridge Univ. Press, New York, 1996.
70. Yee, K., Numerical solution of initial boundary value problems involving Maxwell's equations in isotropic media. *IEEE Transactions on antennas and propagation*, 14(3):302-307, 1966.
71. Yee, K.S., Chen, J.S. and Chang, A.H., Conformal finite-different time-domain (FDTD) with overlapping grids. *IEEE Transactions on Antennas and Propagation*, 40(9):1068-1075, 1992.
72. Draine, B.T. and Flatau, P.J. The Discrete Dipole Approximation for periodic targets: I. theory and tests. *J.Optical Society of America A,* 25(11):2693-2703, 2008.
73. Purcell, E.M. and Pennypacker, C.R., Scattering and absorption of light by nonspherical dielectric grains. *The Astrophysical Journal*, 186:705-714, 1973.
74. Draine,B.T. and Flatau,P.J. User Guide to the Discrete Dipole Approximation Code DDSCAT7.3.0, 2013. url: https://arxiv.org/abs/1305.6497.
75. Draine, B.T. and Flatau, P.J., Discrete-dipole approximation for scattering calculations. *JOSA A*, 11(4):1491-1499, 1994.

76. Draine, B.T., The discrete-dipole approximation and its application to interstellar graphite grains. *The Astrophysical Journal*, 333:848-872, 1988.
77. Singham, S.B., Coupled dipoles in light scattering by randomly oriented chiral particles. *The Journal of chemical physics,* 88(3):1522-1527, 1988.
78. Okamoto, H. and Xu, Y.L., Light scattering by irregular interplanetary dust particles. *Earth, planets and space*, 50(6-7):577-585, 1998.
79. Waterman, P.C., Matrix formulation of electromagnetic scattering. *Proceedings of the IEEE*, 53(8):805-812, 1965.
80. Waterman, P.C., Scattering by dielectric obstacles (Integral equation method for electromagnetic scattering by perfectly conducting obstacles modified for volume scattering regions involving disparities in dielectric constant, permeability or conductivity). *Alta Frequenza*, 38:348-352, 1968.
81. Strom, S. and Zheng, W.E.N.X.I.N., The null field approach to electromagnetic scattering from composite objects. *IEEE transactions on antennas and propagation*, 36(3):376-383, 1988.
82. Lakhtakia, A., Varadan, V.K. and Varadan, V.V., Scattering and absorption characteristics of lossy dielectric, chiral, nonspherical objects. *Applied Optics*, 24(23):4146-4154, 1985.
83. Varadan, V.V. and Varadan, V.K., Multiple scattering of electromagnetic waves by randomly distributed and oriented dielectric scatterers. *Physical Review D*, 21(2):388, 1980.
84. Mishchenko, M.I., Travis, L.D. and Mackowski, D.W., T-matrix computations of light scattering by nonspherical particles: a review. *Journal of Quantitative Spectroscopy and Radiative Transfer*, 55(5):535-575, 1996.
85. Mishchenko, M.I., Travis, L.D., and Lacis, A.A. *Scattering, Absorption, and Emission of Light by Small Particles,* Cambridge University Press, Cambridge, 2002.
86. Barber, P.W., and Hill, S.C. *Light Scattering by Particles: Computational Methods World Scientific,* Singapore, 1990.

87. Liou, K.N. and Hansen, J.E., Intensity and polarization for single scattering by polydisperse spheres: a comparison of ray optics and Mie theory. *Journal of the Atmospheric Sciences*, 28(6):995-1004, 1971.
88. Wendling, P., Wendling, R. and Weickmann, H.K., Scattering of solar radiation by hexagonal ice crystals. *Applied Optics*, 18(15):2663-2671, 1979.
89. Mishchenko, M.I., Light scattering by randomly oriented axially symmetric particles. *JOSA A*, 8(6):871-882, 1991b.
90. Hovenier, J.W., Lumme, K., Mishchenko, M.I., Voshchinnikov, N.V., Mackowski, D.W. and Rahola, J., Computations of scattering matrices of four types of non-spherical particles using diverse methods. *Journal of Quantitative Spectroscopy and Radiative Transfer*, 55(6):695-705, 1996.
91. Gogoi, A., Borthakur, L.J., Choudhury, A., Stanciu, G.A. and Ahmed, G.A., Detector array incorporated optical scattering instrument for nephelometric measurements on small particles. *Meas. Sci. Technol.*, 20(9):095901, 2009.
92. Li, C., Kattawar, G.W. and Yang, P., Effects of surface roughness on light scattering by small particles. *Journal of Quantitative Spectroscopy and Radiative Transfer,* 89(1-4):123-131, 2004.
93. Anderson, T.L. and Ogren, J.A., Determining aerosol radiative properties using the TSI 3563 integrating nephelometer. *Aerosol Science and Technology*, 29(1):57-69, 1998.
94. Black, D.L., McQuay, M.Q. and Bonin, M.P., Laser-based techniques for particle-size measurement: a review of sizing methods and their industrial applications. *Progress in energy and combustion science*, 22(3):267-306, 1996.
95. Hansen, M.Z. and Evans, W.H., Polar nephelometer for atmospheric particulate studies. *Applied optics*, 19(19):3389-3395, 1980.